Force Calculation for General Interatomic Potential

We define a general potential composed of a repulsive pairwise function $\phi(r)$ and an attractive many-body term dependent on the square root of the local density ρ.

Definitions

Let the total potential energy V_{total} be defined as:

$$V_{total} = \left[\sum_{i,j\neq i} \phi(r_{ij}) - \sum_i \sqrt{\rho_i} \right] \tag{1}$$

Where the local density ρ_i is a sum of arbitrary density functions $\psi(r)$:

$$\rho_i = \sum_{j\neq i} \psi(r_{ij}) \tag{2}$$

The distance vectors are defined as $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$, with magnitude $r_{ij} = |\vec{r}_{ij}|$.

The gradient of the distance r_{ij} with respect to the coordinates of atom k is given by:

$$\nabla_k r_{ij} = \frac{\vec{r}_{ij}}{r_{ij}}(\delta_{jk} - \delta_{ik}) \tag{3}$$

Derivation

The force on atom k, denoted as $\vec{F}_k$, is the negative gradient of the potential with respect to the coordinates of atom k:

$$\vec{F}_k = -\nabla_k V_{total}$$

Applying the gradient operator ∇_k:

$$\begin{aligned}
\vec{F}_k &= -\nabla_k \left[\sum_{i,j} (1-\delta_{ij})\phi(r_{ij}) - \sum_i \sqrt{\sum_j (1-\delta_{ij})\psi(r_{ij})} \right] \\
&= -\left[\sum_{i,j} (1-\delta_{ij})\phi'(r_{ij})\nabla_k r_{ij} - \sum_i \frac{1}{2\sqrt{\rho_i}} \nabla_k \rho_i \right] \\
&= -\Bigg[\sum_{i,j} (1-\delta_{ij})\phi'(r_{ij})\frac{\vec{r}_{ij}}{r_{ij}}(\delta_{jk} - \delta_{ik}) \\
&\quad - \sum_i \frac{1}{2\sqrt{\rho_i}} \sum_j (1-\delta_{ij})\psi'(r_{ij})\frac{\vec{r}_{ij}}{r_{ij}}(\delta_{jk} - \delta_{ik}) \Bigg] \\
&= -\Bigg[\sum_j (1-\delta_{kj})\phi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}}(\delta_{jk} - 1) + \sum_{i\neq k,j} (1-\delta_{ij})\phi'(r_{ij})\frac{\vec{r}_{ij}}{r_{ij}}(\delta_{jk}) \\
&\quad - \sum_i \frac{1}{2\sqrt{\rho_i}} \left((1-\delta_{ik})\psi'(r_{ik})\frac{\vec{r}_{ik}}{r_{ik}}(1-\delta_{ik}) + \sum_{j\neq k} (1-\delta_{ij})\psi'(r_{ij})\frac{\vec{r}_{ij}}{r_{ij}}(-\delta_{ik}) \right) \Bigg]
\end{aligned}$$

Grouping by index k and simplifying (resolving the remaining deltas):

$$\vec{F}_k = -\left[\sum_{j\neq k}\phi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}}(-1) + \sum_{i\neq k}\phi'(r_{ik})\frac{\vec{r}_{ik}}{r_{ik}}\right.$$
$$\left. + \frac{1}{2}\left[\sum_{i\neq k}\frac{1}{\sqrt{\rho_i}}\psi'(r_{ik})\frac{\vec{r}_{ik}}{r_{ik}} + \frac{1}{\sqrt{\rho_k}}\sum_{j\neq k}\psi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}}(-1)\right]\right]$$

Using the property that $\vec{r}_{ik} = -\vec{r}_{ki}$ (and thus $\frac{\vec{r}_{ik}}{r_{ik}} = -\frac{\vec{r}_{ki}}{r_{ki}}$) to unify terms:

$$\vec{F}_k = -\left[-\sum_{j\neq k}\phi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}} + \sum_{i\neq k}\phi'(r_{ik})\left(-\frac{\vec{r}_{ki}}{r_{ki}}\right)\right.$$
$$\left. + \frac{1}{2}\left[\sum_{i\neq k}\frac{1}{\sqrt{\rho_i}}\psi'(r_{ik})\left(-\frac{\vec{r}_{ki}}{r_{ki}}\right) - \sum_{j\neq k}\frac{1}{\sqrt{\rho_k}}\psi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}}\right]\right]$$

Renaming index $i \to j$ in the second sums to match terms:

$$\vec{F}_k = -\left[-\sum_{j\neq k}\phi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}} - \sum_{j\neq k}\phi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}}\right.$$
$$\left. - \frac{1}{2}\sum_{j\neq k}\left(\frac{1}{\sqrt{\rho_j}} + \frac{1}{\sqrt{\rho_k}}\right)\psi'(r_{kj})\frac{\vec{r}_{kj}}{r_{kj}}\right]$$

Final Result

$$\vec{F}_k = -\sum_{j\neq k}\left[-2\phi'(r_{kj}) + \frac{1}{2}\left(\rho_j^{-1/2} + \rho_k^{-1/2}\right)\psi'(r_{kj})\right]\frac{\vec{r}_{kj}}{r_{kj}} \tag{4}$$

(Note: The negative sign from the repulsive term cancels with the outer negative gradient, resulting in a positive repulsive force contribution if ϕ' is negative).

Simplifying signs:

$$\vec{F}_k = \sum_{j\neq k}\left[2\phi'(r_{kj}) - \frac{1}{2}\left(\rho_j^{-1/2} + \rho_k^{-1/2}\right)\psi'(r_{kj})\right]\frac{\vec{r}_{kj}}{r_{kj}} \tag{5}$$

Where:

- $\phi'(r) = \frac{d\phi}{dr}$
- $\psi'(r) = \frac{d\psi}{dr}$